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(54) Process for preparing solid components of catalysts, or precursors of such components, in the form of microspheroidal particles, suitable for the preparation of ethylene polymers.

(57) Solid components of catalysts for the (co)polymerization of ethylene, or precursors of such components are prepared by treating (a) an emulsion in a perfluoropolyether of a liquid compound of magnesium, of titanium or of another transition metal, or of solutions thereof, optionally using an electron-donor compound, with (b) a reducing and/or halogenating agent capable of forming an insoluble solid product, after which, if such a product is a precursor of the catalytic component, it is treated with a tetravalent-titanium halide, or with a halide of another transition metal.

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PROCESS FOR PREPARING SOLID COMPONENTS OF CATALYSTS, OR PRECURSORS OF SUCH COMPONENTS, IN THE FORM OF MICROSPHEROIDAL PARTICLES, SUITABLE FOR THE PREPARATION OF ETHYLENE POLYMERS

The present invention relates to emulsions in perfluoropolyether oil of liquid compounds of titanium or other transition metals, and/or magnesium, and to a process for preparing a solid catalytic component, or a precursor of said catalytic component, in the form of microspheroidal particles. In particular, the invention relates to the preparation of solid catalytic components, comprising compounds of magnesium and of titanium, and optionally electro-donor compounds, to be used in the polymerization of ethylene or in the copolymerization of ethylene with minor amounts of one or more alpha-olefins.

Several processes for the preparation of solid catalytic components, suitable for the polymerization of ethylene, and of its mixtures with alpha-olefins are known from the prior art; said catalytic components comprise, as essential constituants, halogenated compounds of magnesium, titanium, and an electron-donor compound. The polymers obtained by use of such catalysts are generally in the form of a powder, with a more or less wide distribution of particle dimensions.

The use of such catalysts is, however, limited from the view point of the separation and of the carriage of the polymers, of the conditions of suspension polymerization, of the conditions of stabilization, and of the conditions of recovery of the polymer in the gas-phase polymerization processes.

There is thus a need for producing available catalysts presenting a high activity, which allow polymers to be obtained in the form of particles having a narrow granulometric distribution, and furthermore presenting a high bulk density.

Various methods have been proposed in the prior art for preparing such catalysts. One of them is disclosed, e.g., in European patent application n° 79102780.8, filed in the name of the present Applicant, and consists in reacting a compound of Ti with a support consisting of, or comprising, an anhydrous Mg halide, in the form of spherical particles having an average diameter of 1-100 microns, a surface area greater than 500 m^2/g, and a porosity higher than 0.5 cm^3/g, and optionally also with an electron-donor compound. A solid catalytic component is thus obtained which, when used with Al-organometallic compounds, produces s polymers in the form of particles having a narrow granulometric distribution, and presenting high free-flowing properties. However, in that case the technology to be used is rather complex.

Another method is disclosed in European patent application n° 83074 also filed in the name of present Applicant, and consists in preparing an emulsion, in a hydrocarbon or in a silicon oil, of an immiscible liquid comprising a complex of $MgCl_2$ with $AlCl_3$ and with toluene and in reacting such an emulsion with Al-trialkyl, to precipitate a solid catalytic component. The catalysts obtained from such catalytic components allow the obtention of polymers in the form of particles presenting a narrow granulometric distribution, the bulk density of which is, however, still not satisfactory.

The process according to the present invention for the preparation of solid components of polymerization catalysts, or of precursors of such components, consists in reacting

(a) an emulsion in a perfluoropolyether of a liquid compound of Mg or of Ti, or of another transition metal, or of their solutions in a solvent not miscible with the perfluoropolyether, with

(b) a reducing and/or halogenating agent capable of precipitating such compounds in the form of a solid product the molecule of which contains at least one Mg-halogen bond and/or one transition metal-halogen bond, in case where compounds of Mg and/or of a transition metal are present in the emulsion.

By the term "precursors of the solid components of the catalyst", are meant herein those Mg compounds, which contain in their molecule at least one Mg-halogen bond, and preferably one Mg-chlorine bond.

The Mg compounds to be suitably used in the perfluoropolyether emulsion according to the process of the invention, are any magnesium compounds, which are liquid at the emulsifying temperature or which are soluble in a solvent not miscible with the perfluoropolyether, and which are able to produce, by reaction with the precipitating agent b), compounds the molecule of which contains at least one Mg-halogen bond.

The titanium compounds, or compounds of other transition metals to be used according to the invention are tetrahalides, alkoxides or halo-alkoxides of tetravalent titanium; $VOCl_3$ or vanadium acetylacetonates are preferably used.

To that class of compounds belong among others those compounds which have the general formula:

(I) $Mg(OR_1)_{2-n}X_n$ wherein:

R_1 = optionally halogenated C_1 to C_{12} hydrocarbon radical;

X is a halogen, preferably chlorine;

n = an integer comprised between 0 and 2, the extremes being included.

Examples of representative compounds of such formula are: $MgCl_2$, $MgBr_2$, MgI_2, $Mg(OC_2H_5)Cl$, $Mg(OC_6H_5)Cl$, $Mg(OC_8H_{17})Cl$, $Mg(OCH_2C_6H_5)Cl$, $Mg(OC_3H_6Cl)Cl$, $Mg(OC_3H_5Cl_2)Cl$, Mg(O-cyclohexyl)Cl, and the mixtures of such compounds; or

(II) $Mg(OR_1)_{m-n}(R_2)_n$ wherein:

R_1 has the above meaning;

R_2 can be a C_1 to C_{12} hydrocarbon radical, similar to or different from R_1;

m and n are integers comprised between 0 and 2, with the extremes being included;

or

(III) $MgX_2.nTi(OR_1)_4$ wherein:

X = halogen, preferably chlorine;

R_1 has the meaning given in formula (I);

n = integer greater than or equal to 2, but preferably not higher than 3.

(IV) Complexes of MgX_2 (wherein X has the above meaning) with electron-donor compounds.

As mentioned herein-above, the compounds of magnesium, titanium and other transition metals can be used for the preparation of their emulsion in perfluoropolyether, in the form of solution in one or more solvents. Such solvents should not be miscible with the perfluoropolyether used. Preferred solvents, in the case of magnesium compounds, are the Ti-alkoxides or halo-alkoxides of general formula:

(V) $Ti(OR_1)_{4-n}X_n$ wherein:

R_1 has the meaning given in above formula (I), and is, in particular, an alkyl, aryl, aralkyl or cycloalkyl radical, optionally containing up to 3 substituent halogen atoms;

X is a halogen, preferably chlorine;

n is an integer comprised between 0 and 3, with the extremes being included.

Examples of such Ti compounds are $Ti(O\text{-}iC_3H_7)_4$, $Ti(O\text{-}nC_4H_9)_4$, $Ti(O\text{-}iC_4H_9)_4$, $Ti(O\text{-}iC_8H_{17})_4$, $Ti(O\text{-}CH_2C_6H_5)_4$, $Ti(O\text{-}C_3H_6Cl)_4$, $Ti(O\text{-}C_3H_5Cl_2)_4$, $Ti(O\text{-}C_4H_9)_3Cl$, $Ti(O\text{-}C_4H_9)_2Cl_2$.

Polymers of the compounds of general formula (V), with a polymerization degree of from 2 to 20, can also be used. Mixtures of the above-mentioned solvents with organic solvents, e.g., hydrocarbon solvents, can be used.

When the liquid Mg compound can react with the precipitating agent, so that it precipitates from the emulsion in the form of a solid compound the molecule of which contains at least one Mg-halogen bond, the presence of liquid Ti compounds in the emulsion is optional. When the Mg compound cannot react with the precipitating agent, it is suitable to use in the emulsion a liquid Ti compound, able to bind itself to the Mg compound, and to react, in its turn, with the precipitating agent, yielding a solid product the molecule of which contains at least one Mg-halogen and Ti-halogen bond. In this second case, the Ti compound can also act as a solvent for the Mg

compound. For example, in case where as Mg compound is used a dihalide, satisfactory results are obtained by using in the emulsion a Ti-alkoxide, which forms a liquid complex with the Mg halide, capable of reacting with the precipitating agent. Such a Ti-alkoxide can be one of those comprised in the above disclosed general formula (V).

The perfluoropolyethers herein used for preparing the emulsions are well-known products, wherein the perfluoropolyether structure is generally formed of recurring C_2F_4O- and/or C_3F_6O- units, optionally also comprises $-CF_2O$- units, as disclosed, e.g., in the patents to which reference is made hereunder.

Examples of suitable perfluoropolyethers are in particular those which conform to the following formulae, and have a viscosity comprised between 4 and 1500 cSt:

A) $CF_3O-(C_3F_6O)_m(C_2F_4O)_n(CFXO)_q-CF_3$
wherein X is -F or $-CF_3$; m, n and q are integers, the m/n + q ratio being comprised between 1 and 50 and n/q comprised between 1 and 10; the oxyperfluoroalkylene units are randomly distributed along the chain.
The preparation of these compounds is disclosed in U.S. patent 3,665,041.

B) $C_3F_7O(C_3F_6O)_m-R_f$
wherein R_f is C_2F_5 or C_3F_7 and m is an integer greater than 2.
The preparation of these compounds is disclosed in U.S. patent 3,242,218.

C) $CF_3O(C_2F_4O)_p(CF_2O)_q-CF_3$
wherein p and q are integers equal to, or different from each other, and the p/q ratio is comprised between 0.5 and 1.5; the oxyperfluoroalkylene units are randomly distributed along the chains.
The preparation of these compounds is disclosed in U.S. patents 3,715,378 and 3,665,041.

D) $CF_3O(C_3F_6O)_m(CFXO)_n-CF_2Y$
wherein X and Y, equal to or different from each other, are -F or $-CF_3$; m and n are integers and the m/n ratio varies between 5 and 40. The oxyperfluoroalkylene units

are randomly distributed along the chain.

The preparation of these compounds is disclosed in U.K.patents 1,104,481 and 1,226,566.

E) The perfluoropolyethers with oxethanic structure are disclosed in Italian patent application 19494 A/85.

F) $R'_fO(CF_3CF_2O)_pR_f$

wherein R_f and R'_f, equal to or different from each other, are $-CF_3$ or $-C_2F_5$ and p is an integer such that the viscosity is within the previously indicated limits. Products of this type are disclosed in U.S. patent 4,523,039.

G) $R'_fO(CF_2CF_2CF_2O)_sR_f$

wherein R_f and R'_f, equal to or different from each other, are $-CF_3$ or $-C_2F_5$ and s is an integer such that the viscosity is within the previously indicated limits. Products of this type are disclosed in European patent application 148 482.

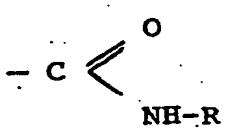
Usually, the perfluoropolyether used for forming the emulsion has a viscosity comprised between 4 and 200 cSt.

Although the process is normally carried out with the emulsion at room temperature, operating at a value lower or higher than room temperature, e.g. at a temperature from -30° to +90°C, is however possible.

The ratio, by volume, of the magnesium compound to the perfluoropolyether in the emulsion is comprised between 0.01 and 1.

The emulsion is preferably prepared in the presence of an emulsion stabilizer constituted by a perfluoropolyether having a functionalized terminal.

The perfluoropolyether having a functionalized terminal has preferably the following terminals:



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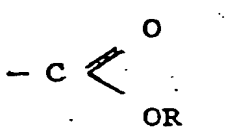

diethyl-n-butyl-malonate, diethyl-n-dibutyl-malonate, diethyl-phenyl-malonate, diisobutyl-adipate, dioctyl-sebacate, alkyl-maleates, alkyl-aryl-maleates, alkyl- or aryl-alkyl-pivalates, alkyl-acrylates and metacrylates, phthalates, such as isobutyl-, diisobutyl-, dioctyl- or neopentyl-phthalate, diethyl-phthalate, diphenyl-phthalate, benzyl-butyl-phthalate; diphenylcarbonate, ethyldiphenylacetate, isobutyl-benzoylacetate, 1,2-dihydroxy-diacetato-benzene, diisobutyl-2,3-naphthalene-dicarboxylate.

Among ethers, for exemplifying purposes can be cited the following: the C_2 to C_{20} mono-, di-, tri- or tetra-ethers, such as diethylether, dibutylether, diisoamylether, dioctyl-ether, dioxan, trioxan, tetrahydrofuran, ethyleneglycol-di-methylether, propylene oxide, epichlorohydrin, benzophenone.

Examples of other electron donors which can be used are phosphites, such as triphenylphosphite, triphenylphosphine, 1,4-butanediol; $POCl_3$, acetyl alpha-methyl-alpha-phenyl chloride, benzoyl chloride, bromide and iodide, toluyl chloride, butyrolacton, and generally all those indicated in European patent applications n° 86471, 86742 and 86743 in the present Applicant's name. Furthermore, the silicon compounds and the heterocyclic compounds containing at least one nitrogen atom are indicated.

The precipitating agents (b) to be used for the treatment of the emulsion, can be any halogenated compounds capable of reacting with the compound of magnesium or of the transition metal contained in the emulsion to yield a solid compound the molecule of which contains at least one Mg-halogen bond, and/or at least one transition metal-halogen bond. In the case of emulsions containing Mg compounds, the compounds to be used are generally halogenating compounds capable of forming, in the reaction with Mg, Mg halides, or organometallic compounds, in particular aluminum-trialkyls, able to decompose the liquid Mg complex, with the formation of Mg halide. In the case of transition metals, the precipitating agent is generally a organometal reducer.

Examples of halogenating compounds are the silicon compounds having the general formula:

$$SiR_xX_{4-x}$$

wherein:

R is a C_1 to C_{20} linear, branched or cyclic alkyl, or a C_7 to C_{20} alkylaryl; R may also contain heteroatoms, in particular O and/or Si atoms, and substituents, e.g. Cl.

Examples of suitable emulsion stabilizers are:

$$CF_3-(OC_3F_6)_n(OCF_2)_m-O-CF_2-COO-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \quad (I)$$

$$CF_3-(OC_3F_6)_n(OCF_2)_m-OCF_2-COO-CH_2-CHOH-O-(CH_2)_3-Si(OMe)_3 \quad (II)$$

$$CF_3-(OC_3F_6)_n(OCF_2)_m-O-CF_2CO-NH-(CH_2)_3-Si(OEt)_3 \quad (III)$$

The amount of emulsion stabilizer is generally comprised between 0.01% and 5% by weight relative to the perfluoropolyether; however any amounts allowing the emulsion to be obtained can be used in the process of the invention.

The emulsion can be prepared, e.g., by a strong stirring, e.g., by using an Ultraturrax stirrer.

Electron-donor compounds can be added to the emulsion of Mg compound, prior to the treatment thereof with the precipitating agent (b).

Particularly suitable electron-donors contain in their molecule oxygen atoms, or sulphur, phosphorus or nitrogen or silicon atoms.

In particular, the following can be cited: esters of oxygen-containing acids, acid halides, ketones, aldehydes, alcohols, ethers, thioethers, amides, lactons, phosphines, phosphoroamides, silicon compounds, such as silanic and siloxanic compounds.

Among esters, for exemplifying purposes can be cited the following: the C_1 to C_{20} alkyl esters of aromatic, aliphatic or aromatic mono- or polycarboxy acids, in particular the mono- and polyesters of the saturated and unsaturated polycarboxy acids, the esters of the aromatic hydroxyacids, and in general those disclosed, as electron-donors, in published European patent applications n° 45976, 45977, in the name of the present Applicant. Examples of such esters are methyl-, ethyl-, butyl- or octyl-acetate; ethyl- or ethylphenyl-butyrate, ethyl-valerianate, phenyl-propionate, mono- and di-ethyl-succinate, ethyl-methyl-, ethyl-, propyl- or octyl-benzoate, ethyl-p-toluate, ethyl-p-anisate, diethyl-diisobutyl-malonate,

wherein:

R = C_1 to C_{20} alkyl, aryl, aralkyl or alkoxy radical;

X = halogen, preferably chlorine; and

$0 \leq x \leq 3$;

or the titanium compounds of general formula:

$$Ti(OR)_xX_{4-x}$$

wherein R, X and x have the above meaning;

or the aluminum compounds, of formula:

$$AlR_xX_{3-x}$$

wherein R and X have the above meaning; and $0 \leq x \leq 2$.

For exemplifying purposes, among these compounds $SiCl_4$, $TiCl_4$, $AlEt_2Cl$ can be cited.

The treatment of the emulsion with the precipitating (or halogenating) agent is carried out by using an amount of said agent at least equal to the stoichiometrical amount necessary to obtain at least one Mg-halogen bond in the molecule of the magnesium compound present in the emulsion, and/or to obtain at least the reduction by one unit of the valence of the transition metal, when a transition metal compound is present.

The treatment temperature is not critical; for exemplifying purposes, operating is possible at temperatures comprised between 20°C and the boiling temperature of the precipitating agent. The treatment can be performed by adding the halogenating agent as such, or diluted in a hydrocarbon solvent, to the emulsion, or vice-versa.

After the reaction, the solid product is separated washed and then, if is was obtained in the form of a precursor (i.e., if it was obtained from the emulsion without Ti compounds, or without any compounds of other transition metals, by using a precipitating agent different from a transition metal compound), it is treated with a tetravalent-Ti halide, or with a halide of a transition metal different from Ti, to obtain the catalytic component. If desired, operating in the presence of an electron donor is possible.

The treatment can also be carried out in the presence of an aromatic or halogenated hydrocarbon solvent. The size of the catalytic component of the precursor is controlled by the

stirring speed, by the viscosity of the polyperfluoroether liquid and of the liquid, or solution of compound of Mg and/or of the transition metal. In particular, the size decreases with increasing stirring speed.

The following examples are supplied for the purpose of illustrating the present invention, without constituting a limitation thereof.

EXAMPLE 1

Into a 1000 ml autoclave equipped with a magnetic-anchor stirrer and a dip tube connected, through a valve, to a 4000 mm long steel pipe of 2.4 mm of inner diameter, are charged 300 ml of perfluoropolyether (Epilden D1/LS® by Montefluos S.p.A.), having a viscosity of 4 cSt, 40 ml of a liquid having the composition $MgCl_2.2Ti(OC_4H_9)_4$ (equivalent to 60 mM of Mg), and 6 ml of anhydrous n-heptane. The mass is maintained under stirring at 400 rpm, for 10 minutes, after which an overpressure of 50 atm of N_2 is created. During a 60 second period, the emulsion contained in the autoclave is discharged, through the above-described pipe, into a 1000 ml flask, containing 400 ml of $TiCl_4$, maintained under stirring. The whole operation is carried out at 20°C. The reaction mass is maintained under stirring in the flask for 10 minutes, and the suspension is then transferred through a fritted filter into a reactor, wherein it is allowed to react at 100° for 2 hours. $TiCl_4$ is filtered off, and an equal amount thereof is added. The mixture is left to react at 120°C for 2 hours. The suspension is filtered and is washed with portions of 300 l of n-heptane at 90°C, until no further chlorine ions are present in the filtrate.

Upon analysis, the solid obtained shows a titanium content of 2.5%.

The ethylene polymerization test carried out by using 12 mg of the solid thus obtained as catalytic component gave the following results.

- polymer ..... 384 g
- yield ..... 32.0 kg of polymer/catalyst g.
- $[\eta]$ ..... 2.10 dl/g
- flowability index (flow). 21 seconds

. compacted bulk density
(C.B.D.) ..... 0,43 g/cc

EXAMPLE 2

Into the autoclave as described in example 1, are charged 500 ml of perfluoropolyether and 200 ml of an 0.4 M solution of $Mg(n\text{-hexyl})_2$ in heptane.

The mass is stirred and, according to the same procedure as described in example 1, the contents of the autoclave are discharged, through the pipe, into a flask containing 400 ml of $SiCl_4$, maintained understirring. The reaction is allowed to proceed for 10 minutes at 25°C and 2 hours at 60°C. The solid formed, after filtration and washing with n-heptane, is reacted with 100 ml of $TiCl_4$ at 185°C for 2 hours, after which it is isolated by filtration and washed with h-heptane until the chlorine ions disappear from the filtrate. Upon analysis, the solid obtained shows a titanium content of 1.2%.

The ethylene polymerization test carried out by using 18 mg of the solid thus obtained as the catalytic component gave the following results:

. polymer ..... 315 g
. yield ..... 8.2 kg of polymer/catalyst g.
. [η] ..... 2.10 dl/g
. flowability index ..... 19 seconds
. compacted bulk density .. 0.44 g/cc

COMPARATIVE EXAMPLE 1

Example 1 is repeated without any use of perfluoropolyether and hence the emulsifying step is omitted. Upon analysis, the solid thus obtained shows a titanium content of 2.6%. The ethylene polymerization test carried out by using 13 mg of the solid thus obtained as the catalytic component gave the following results:

. polymer ..... 410 g
. yield ..... 31.5 kg of polymer/catalyst g.
. [η] ..... 2.0 dl/g
. flowability index ..... 26 seconds
. compacted bulk density .. 0.31 g/cc

COMPARATIVE EXAMPLE 2

Example 2 is repeated without any use of perfluoropolyether and hence the emulsifying step is omitted. Upon analysis, the solid thus obtained shows a titanium content of 1.25%. The ethylene polymerization test carried out by using 18 mg of the solid thus obtained as the catalytic component gave the following results:

- polymer ..... 290 g
- yield ..... 18.1 kg of polymer/catalyst g.
- [η] ..... 2.15 dl/g
- flowability index ..... 28 seconds
- compacted bulk density .. 0.28 g/cc

The polymerization conditions prevailing in the above examples were the following.

A proper amount of the catalytic component prepared according to the examples was charged, together with 1000 ml of anhydrous n-heptane, containing 5 mmol of aluminumtriisobutyl, under a nitrogen atmosphere, into a stainless-steel autoclave having a 3-liter capacity, equipped with a magnetic-anchor stirrer and heated to the temperature of 85°C.

4 atm of hydrogen and 9 atm of ethylene were added and the total pressure was maintained constant throughout the polymerization operation by continuously feeding ethylene.

After three hours of reaction, the polymerization was discontinued, the polymer was filtered off and dried.

C L A I M S

1.- Emulsions in polyperfluoroether oil of compounds, liquid under emulsifying conditions, of magnesium and/or of a transition metal, or of solutions of compounds of Mg and/or of a transition metal in solvents not miscible with perfluoropolyether.

2.- Process for the preparation of a solid catalytic component, suitable for use in the polymerization of ethylene or of mixtures thereof with minor amounts of alpha-olefins, or of a precursor of such a catalytic component, in the form of microspheroidal particles, which consists reacting
(a) an emulsion in a perfluoropolyether of compounds of magnesium, and/or of a transition metal, either liquid or in solution in a solvent not miscible with such a perfluoropolyether, optionally in the presence of electron-donors, with
(b) an agent able to precipitate such a compound in the form of a solid, the molecule of which contains at least one transition metal-halogen bond and/or one Ti-halogen bond, in the case where compounds of a transition metal are present in the emulsion.

3.- Process according to claim 1, wherein the magnesium compound is in the form of a solution in a liquid of titanium compound.

4.- Process according to claims 1 and 2, wherein Mg compound presents the general formula:

(I) $Mg(OR_1)_{2-n}X_n$

wherein:
R_1 = a C_1 to C_{12} ~~optionally halogenated~~ hydrocarbon radical;
X = a halogen;
n = an integer comprised between 0 and 2.

5.- Process according to claims 1 and 2, wherein Mg compound presents general formula:

(II) $Mg(OR_1)_{m-n}(R_2)_n$

wherein:
R_1 = a C_1 to C_{12} optionally halogenated hydrocarbon radical;
R_2 = a C_1 to C_{12} hydrocarbon radical equal to, or different from R_1;
m and n = integers comprised between 0 and 2.

6.- Process according to claims 1 and 2, wherein Mg compound presents general formula:

(III) $MgX_2.nTi(OR_1)_4$

wherein:

X = a halogen;

R = a C_1 to C_{12} optionally halogenated hydrocarbon radical;

n = an integer greater than or equal to 2.

7.- Process according to claims from 1 to 5, wherein the solvent of the magnesium compound is constituted by a liquid titanium compound of the general formula:

(IV) $Ti(OR_1)_{4-n}X_n$

wherein:

R = a C_1 to C_{12} optionally halogenated hydrocarbon radical;

X = a halogen;

n = an integer comprised between 0 and 3.

8.- Process according to claim 6, wherein the Mg compound is a Mg halide.

9.- Catalytic compounds and precursors of such components obtained by the process according to preceding claims.

10.- Polymers obtained by using catalytic components obtained by the process according to preceding claims.

0258089

Application Number

EP 87 40 1713

European Patent Office

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	EP-A-0 083 074 (MONTEDISON) * Claims *	1	C 08 F 10/00 C 08 F 4/60
A	US-A-3 953 414 (P. GALLI et al.) * Claim 1 *	1	
A	FR-A-2 434 180 (MONTEDISON) * Claim 1 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 08 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16-11-1987	DE ROECK R.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)